CHEMICAL AND ENERGETIC ASPECTS OF
## CVD DIAMOND GROWTH

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INTRODUCTION

Excitement has emerged in both the scientific and industrial communities with the development of techniques for creating crystalline diamond films and coatings using low pressure gases rather than the high pressures and temperatures previously considered essential.(1) These developments have opened a new era in diamond technology and offer the potential for exploiting diamond's unique properties in applications ranging from coatings for cutting tools, to free standing windows and lense coatings for visible and infrared transmission, to thin films for high temperature, high power semiconductor devices.

Applications requiring advanced materials can uniquely utilize diamond because it (i) is the hardest known material, (ii) has the highest room temperature thermal conductivity of any material, (iii) is resistant to heat, acids, and radiation, (iv) is a good electrical insulator, but can be doped to produce either p-type or n-type semiconductors, (v) has a small dielectric constant, (vi) has a large hole mobility, and (vii) is transparent to visible and infrared radiation.(1) The high pressure-high temperature (HPHT) synthetic diamonds developed by General Electric in the 1950's (2) are now commonplace in cutting, grinding, and polishing, but many potential applications of diamond require thin films or coatings which cannot be produced from either natural or HPHT synthetic diamonds.

The diamond coating process which has generated the recent excitement utilizes temperature and pressure conditions under which graphite is clearly the stable form of carbon. However, kinetic factors allow crystalline diamond to be produced by a net chemical reaction of:

$$CH_4(g) \xrightarrow[\text{activation}]{} C(\text{diamond}) + 2 H_2(g) \qquad (1)$$
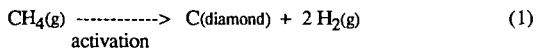
In addition to methane, a wide variety of carbon containing reactant gases can be used. The typical process consists of a reactant gas at less than atmospheric pressure which contains >95% hydrogen and is activated by passing it through a plasma or past an ~2000°C filament before contacting an 800-1000°C substrate on which the diamond is deposited.

Many questions must be answered concerning this deceivingly simple looking "metastable" process before the potential of the new coating technology can be realized. Our understanding of the basic science must be extended far beyond our present knowledge, a challenge currently being met by laboratories around the world. The aim of this article is to sumarize our current understanding of the chemical and energetic aspects of the growth processes for crystalline diamond.

CHEMICAL OBSERVATIONS

Many experimental observations concerning the activated vapor deposition of crystalline diamond have been made, particularly by Russian scientists Derjaguin, Fedoseev, Spitsyn, and co-workers. They have developed an extensive experimental base of chemical and kinetic information, and have proposed global kinetic theories for diamond growth based on nucleation theory, Langmuir adsorption-desorption kinetics, and equilibrium. Recent reviews in English give excellent summaries of this work.(1,3-5)

A major problem in growing high–quality diamond films is the co-deposition of graphitic-like carbon. Derjaguin and co-workers experimentally determined that the addition of excess hydrogen to the hydocarbon precursor gas led to less graphite co-deposition with crystalline diamond, and that "activating"

the precursor gas prior to deposition increased the diamond growth rates from Å/hour to μm/hour. They activated the gas using either an electric discharge in the system, or a hot tungsten filament over which the gas flowed before encountering the lower temperature deposition region. A manifestation of the competition between the growth of diamond and graphite is the temperature dependence of the diamond growth rate which exhibits a maximum near 1000°C.

Derjaguin and Fedoseev(6) made a major breakthrough in determining that atomic hydrogen is critical to achieving appreciable growth rates for crystalline diamond, and proposed that a super-equilibrium concentration of atomic hydrogen at the growth surface is responsible for the major reduction in graphite co-deposition. They argue that atomic hydrogen behaves like a 'solvent' for graphite. Their studies of the relative etching rates of diamond and graphite showed that the removal of graphite by 'activated' hydrogen was orders of magnitude faster than diamond. Setaka(7) recently reported etching rates of graphite, glassy carbon, and diamond in a hydrogen plasma under typical diamond growth conditions. In units of mg/cm^2-hr, his values are 0.13 for graphite, 0.11 for glassy carbon, and 0.006 for diamond. Saito et al.(8) also showed much greater etching rates for graphite than diamond when subjecting the materials to microwave plasmas of either hydrogen, or hydrogen-1.6%water mixtures.

Derjaguin and co-workers also observed that the nature of the precursor hydrocarbon gas had little effect on the deposition behavior. Sato et al.(9) have grown diamond from gaseous mixtures of various hydrocarbons and hydrogen by plasma-assisted deposition and found similar results. Both saturated and unsaturated hydrocarbons were used, and similar growth features were noted for all the hydrocarbons when comparisons were made as a function of the C/H ratio in the input gas. The density of nucleation and the growth rates were found to be essentially the same as those observed with the more commonly used methane. Crystalline diamond has been grown using aliphatic and aromatic hydrocarbons as well as alcohols and ketones. Small amounts of O_2 added to the precursor gas accelerates the growth rate of diamond films. Diamond can also be grown from hydrogen / hydrocarbon gas mixtures which contain larger amounts of oxygen (as in an oxygen-acetylene flame).

The relative independence of diamond growth on the nature of the input hydrocarbon species is consistent with the fact that most hydrocarbon sources tend to chemically transform to common product species (such as acetylene, one of the most stable of such gaseous products) under harsh environments such as those found in high temperature pyrolysis(10,11), combustion(12), plasmas(13), and the other typical methods used for activating precursor gases in diamond deposition. Good quality diamond films have been produced under a variety of different activation methods: microwave–, rf–, uv–, laser–, and hot–filament activated gas mixtures.(1) Approximately the same growth conditions (temperature, pressure, concentrations of precursors) are needed for crystalline diamond growth, regardless of the method of activation. The method of activation influences the rate of diamond growth, but not the general structure of the deposited crystallites.

A number of ongoing spectroscopic studies of activated methane-hydrogen gas mixtures under diamond film growth conditions indicate a predominance of acetylene and methyl radical growth species. One such study by Celii et al.(14) reported *in situ* infrared diode laser absorption spectroscopy results obtained from examinations of gas phase species present during hot-filament assisted deposition of diamond films; another by Harris et al.(15) reported mass spectra investigations in a hot-filament assisted diamond growth system as a function of filament-to-substrate distance. The initial analysis of these latter authors suggests that diamond growth comes mainly from acetylene and/or methyl radical precursors, but contributions from methane and ethylene cannot be ruled out.

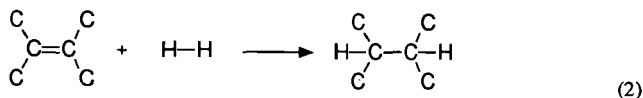## ENERGETICS OF GAS-SOLID GROWTH INTERFACE

The pressure vs. temperature phase diagram for carbon given in Figure 1 clearly shows that graphite is the stable form of carbon under the conditions used for vapor depositing crystalline diamond. Why is it then possible to grow diamond at 750-1100°C and less than atmospheric pressure?

Although an established mechanistic answer is not yet available for the above question, one that is consistent with reported experimental facts can be given(16). The heart of this hypothesis on "metastable" diamond growth rests on the fact that the diamond growth process occurs at the gas–solid interface in the carbon–hydrogen system. The vapor growth process does not involve just elemental carbon, the one component which is represented on the phase diagram, but it also involves hydrogen. A diamond carbon surface saturated with sp^3 C–H bonds is more stable than a carbon surface free of hydrogen. Once a surface carbon is covered by another diamond growth layer, then that covered carbon possessing four sp^3 C–C bonds is metastable with respect to a graphitic carbon. Thus, an upper temperature limit for the vapor growth of diamond is determined by the kinetics of the diamond-to-graphite solid state transformation (and how these kinetics are influenced by structural imperfections).
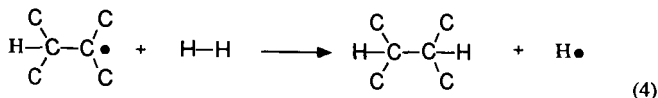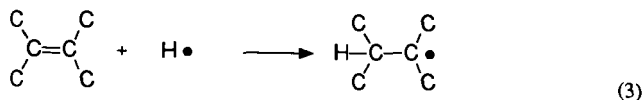
The close relationship between the diamond and graphite crystal structures is depicted in Figure 2. The puckered {111} planes of diamond are shaded to emphasize their relationship to the {001} planes of graphite. Hydrogen atoms are shown as satisfying the "dangling sp^3 bonds" of the carbons on the top diamond plane. Without the hydrogens maintaining the sp^3 character of these surface carbons, it is easy to imagine the {111} diamond planes collapsing into the more stable planar graphite structure during the growth process. In fact, in the absence of hydrogen, it is well known that the surface atoms on cleaned bulk diamond crystals will reconstruct from their bulk-related surface sites at about 900-1000°C. However, in hydrogen, the surface sp^3 bonds are satisfied by C-H bonding.(17-20)

The question then arises as to why earlier thermal CVD studies utilizing hydrogen-methane mixtures for epitaxial growth on diamond surfaces were of very limited success [see, for example, Angus et al.(21)]. The pressure-temperature-composition conditions used by these earlier researchers were quite similar to those currently used for the successful activated vapor growth of crystalline diamond, but the primary deposition product was always graphitic-like carbon in these early studies.

The net saturation of a C=C double bond with hydrogen

$$
\begin{array}{ccc}
\text{C} \quad\;\; \text{C} & & \text{C} \quad\;\; \text{C} \\
\quad\diagdown\;\;\diagup & & \quad\diagdown\;\;\diagup \\
\quad\text{C=C} \quad + \quad \text{H—H} \quad\longrightarrow\quad \text{H—C—C—H} \\
\quad\diagup\;\;\diagdown & & \quad\diagup\;\;\diagdown \\
\text{C} \quad\;\; \text{C} & & \text{C} \quad\;\; \text{C}
\end{array} \tag{2}
$$

yields a favorable negative enthalpy change, ΔH^0(reaction) = -126 kJ. However, an activation energy to produce either a carbon or a hydrogen radical will be required to get the net reaction to proceed at a significant rate. Likely mechanistic radical reactions are

$$
\begin{array}{ccc}
\text{C} \quad\;\; \text{C} & & \text{C} \quad\;\; \text{C} \\
\quad\diagdown\;\;\diagup & & \quad\diagdown\;\;\diagup \\
\quad\text{C=C} \quad + \quad \text{H} \bullet \quad\longrightarrow\quad \text{H—C—C} \bullet \\
\quad\diagup\;\;\diagdown & & \quad\diagup\;\;\diagdown \\
\text{C} \quad\;\; \text{C} & & \text{C} \quad\;\; \text{C}
\end{array} \tag{3}
$$

$$
\begin{array}{ccc}
\text{C} \quad\;\; \text{C} & & \text{C} \quad\;\; \text{C} \\
\quad\diagdown\;\;\diagup & & \quad\diagdown\;\;\diagup \\
\text{H—C—C} \bullet \;+\; \text{H—H} \longrightarrow \text{H—C—C—H} \;+\; \text{H} \bullet \\
\quad\diagup\;\;\diagdown & & \quad\diagup\;\;\diagdown \\
\text{C} \quad\;\; \text{C} & & \text{C} \quad\;\; \text{C}
\end{array} \tag{4}
$$

where a hydrogen radical attacks the C=C double bond to produce a carbon radical, which then reacts with a hydrogen molecule to complete the saturation and regenerate a hydrogen radical. This is in agreement with the fact that only when gas activated deposition methods were first employed in the 1970's did the growth rates of crystalline diamond become large enough to be of technological interest.

As was mentioned in the section on the chemistry of diamond growth, atomic hydrogen etches sp^2 graphitic carbon at a much higher rate than it etches sp^3 diamond carbons. Thus, the source of hydrogen

atoms can serve the dual role of hindering graphite growth as well as etching away any that does nucleate on the growing diamond surface.

The thermodynamics of the deposition process may place a lower limit on the deposition temperature for a given total pressures and gas concentration. Without some type of surface activation such as bombardment, the surface reactions for deposition may approach their thermal equilibrium limits. The fact that faceted diamond crystals are produced during deposition is a typical indication that surface mobilities are large enough for surface reactions to reach equilibrium. Which reactions reach their equilibrium limits, and which ones are kinetically limited is still an open question, but it is still of value to consider the thermodynamic limits for the deposition process.

Two plots of the output of equilibrium calculations are shown in Figure 3 to illustrate how the deposition limits depend on experimental parameters.(16) Such calculations have also be made by Bichler et al.(22) and Sommer et al.(23) The fraction of carbon deposited from methane-hydrogen mixtures is plotted versus temperature for several pressures and compositions. Two important observations can be made:

    (1) The fraction of carbon deposited changes from practically zero at lower
        temperatures to close to 100% over two hundred degrees.

    (2) High pressures and/or low methane concentrations increase the lower
        temperature limit required to obtain any deposit.

Thus, thermodynamic considerations set a lower temperature limit on diamond growth of about 400 – 600°C, depending on specific pressure–composition conditions, unless "non–equilibrium" bombardment techniques are used. These latter techniques always produce some diamond-like carbon (DLC), or similar highly defective form of carbon, along with crystalline or microcrystalline diamond.

Not shown on the above plots is the fact that the elemental gaseous carbon species of C, C_3, C_5, etc. have negligible partial pressures at about 2000°C and lower. Also, at 2000°C, a typical temperature for the filament in the hot-filament-activated systems, the quantity of atomic hydrogen in equilibrium with about 10 torr of molecular hydrogen is close to 7 at. %, an appreciable amount to interact at the 800-1000°C substrate temperature.

CONCLUDING REMARKS

Under the temperature-pressure conditions used for the growth of diamond from the vapor, graphite is clearly the most stable form of carbon. However, the energy differences between depositing diamond and graphite are quite small, so kinetic factors will determine which solid phase is deposited.in the carbon-hydrogen system. Even so, energetic arguements are still important in explaining the experimental observations.

At the solid-gas interface where the diamond nucleation and growth processes are occurring, a diamond surface with hydrogens satisfying the "dangling" sp^3 carbon bonds is energetically more favorable than a graphite surface. If diamond forms during deposition, and its surface is adequately saturated with sp^3 C-H bonds, then graphite can subsequently form only through a solid state transformation, which is kinetically unfavorable until temperatures greater than ~1600°C are reached. If graphite forms during the deposition process, atomic hydrogen can saturate the C=C double bonds to produce a diamond surface with sp^3 carbons, or it can preferentially remove the graphite through a chemical etching process. Without the presence of atomic hydrogen, the rates of saturating surface C=C bonds and the rates of graphite etching are slow compared to the solid carbon deposition, so graphitic-like carbon may dominate the process. This delicate balance between deposition rate and the concentration of atomic hydrogen has not yet been quantitatively measured.

The role of atomic hydrogen in the etching of graphitic-like carbon may be shifted to oxygen in systems containing appreciable amounts of this element, such as in the growth of diamonds from flames.

However, oxygen will probably not be important in stabilizing a diamond surface by saturating the "dangling" sp^3 carbon bonds on such a surface. The experimental and theoretical expertise which has evolved over the years in the area of combustion chemistry is clearly needed to develop quantitative models for the growth of diamond from C-H-O vapor systems.

ACKNOWLEDGMENTS

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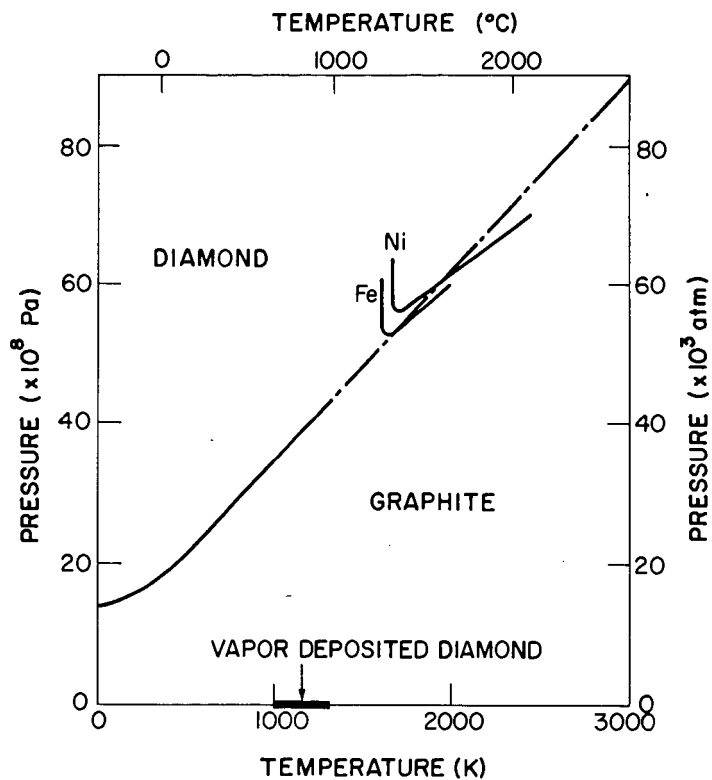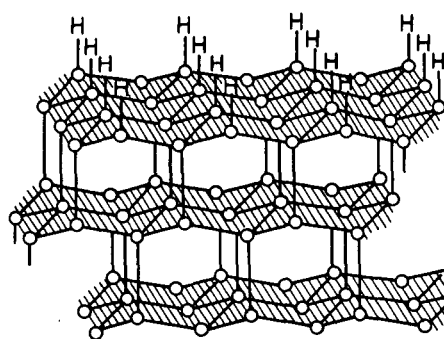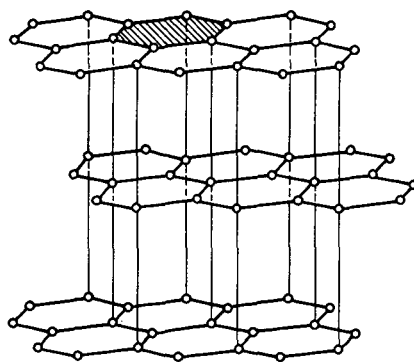
Figure 1: Pressure vs Temperature Phase Diagram for Carbon . The lines labeled with metallic elements denote the high pressure-high temperature (HPHT) conditions utilized for diamond growth using metallic solvents.

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DIAMOND

GRAPHITE

Figure 2: Schematic Diagrams Showing the Similarities in the Crystal Structures of Diamond and Graphite. The hydrogen atoms bonded to the surface carbons depict their role in stabilizing the diamond surface structure.
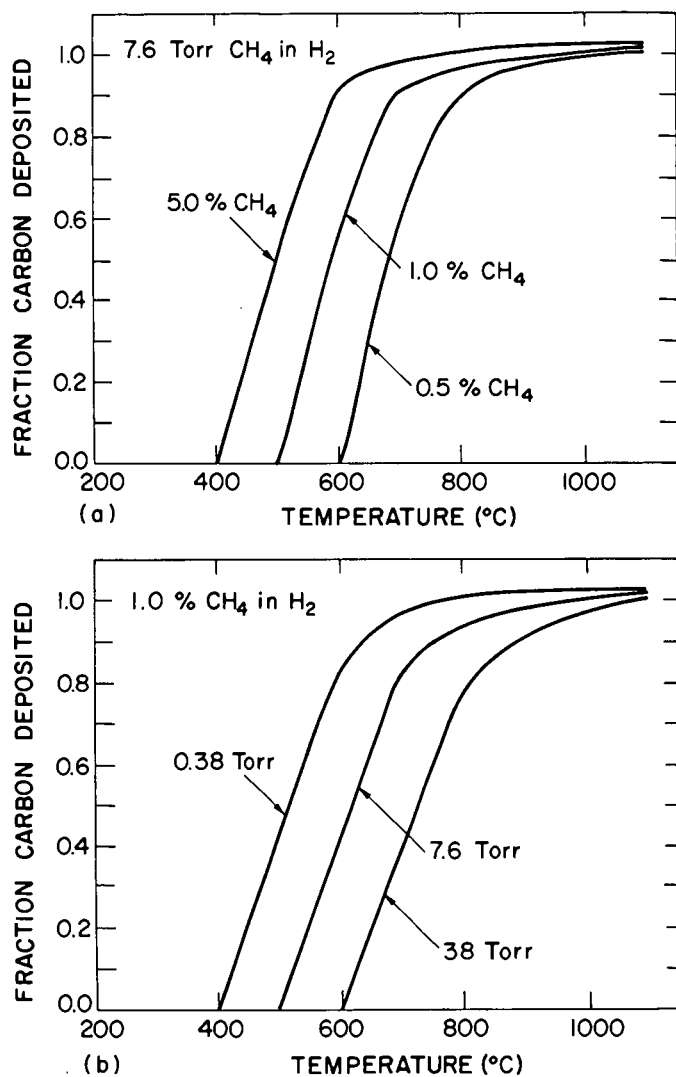
Figure 3: Equilibrium Plots of the Fraction Carbon Deposited from Methane/Hydrogen Mixtures as a Function of Temperature. (a) Constant total pressure, varying CH_4 content in reactant gas (b) Constant CH_4 content, varying total pressure.